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EXPERIMENTAL MEASUREMENT TECHNIQUE FOR

ORGANIC POLYMER FILMS AND CRYSTALS

Advanced Research Projects Agency

Order Number: DAAK70-77-C-004[illegible]

UNIVERSITY of PENNSYLVANIA

DEPARTMENT OF PHYSICS

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Philadelphia, Pennsylvania

EXPERIMENTAL MEASUREMENT TECHNIQUE FOR ORGANIC POLYMER FILMS AND CRYSTALS

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School: College

Department: Physics

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I. Introduction

The primary goal of our present research activity is to systematically design and study high strength crystalline polymers as thin films and single crystals that exhibit high pyroelectric, and nonlinear optical properties. In recent years, modest piezoelectric and pyroelectric response has been shown to exist in some amorphous synthetic organic polymers.[1] On the basis of developments in this field, we have focused on two features that are important: (i) the amorphous structure, and (ii) the actual molecular charge dipole present in these organic polymers. These two features are responsible for limiting the piezo- and pyroactivity to relatively small values in presently available polymers. By going to crystalline polymers and increasing the magnitude of the charged dipole, we believe the optimum response is achievable in organic polymers. Detailed design features and synthetic procedures for new single crystal polymers being developed for these studies will be reported elsewhere.

In this interim report, we briefly describe a convenient experimental apparatus for measuring the low frequency dielectric constants and pyroelectric coefficients of these polymeric solids. The measurement technique can be computer controlled and allows on-line data reduction. First, we summarize the measurement methods adapted for use with polymer samples and then provide a detailed description of the experimental apparatus which has been tested using ferroelectric crystals such as barium titanate ($BaTiO_3$).

Experimental Methods: Pyroelectric and Dielectric Constant

1. Pyroelectric Coefficient

The pyroelectric constant is being measured by a charge integration technique where the sample is a stress-free mounted dielectric material inside a parallel plate capacitor. The method was independently developed by several investigators, especially A. M. Glass.[2]

A simple diagram of the circuit used is shown in Figure 1. The temperature of the sample S is changed from T_2 to T_1 causing a change in the sample polarization $\triangle P$. Charge flows between the plates of the capacitor, which is integrated by the operational amplifier (Keithly 301). The change is related to the change in polarization of the samp_e by the expression

$$V_{out} = [\triangle P]_{T_1}^{T_2} / Z_f$$

From the derivative of this curve, dP/dT, one obtains the components of the pyroelectric coefficient measured along the different crystallographic directions.

2. Dielectric Constant

The dielectric constant is being determined by two capacitance methods which differ in the degree of precision. High precision values are obtained using a General Radio 1615A AC bridge where the measured capacitance of the sample dielectric between two parallel plates yields the sample dielectric constant directly.[3] Measurements are made at a frequency of 1 kHz as a function of temperature.

The second method for determining the dielectric constant is also a charge integration technique where again the sample is a stress-free mounted dielectric material inside a parallel plate capacitor. The circuit used is schematically drawn in Figure 2. The reference capacitor Z_f is known. The gain of the second operational amplifier (Keithly 301) is simply - Z_f/Z_i which is measured by the lock-in amplifier (PAR 124). The sample dielectric constant is obtained from Z_i, the capacitance of the sample. With this technique, measurements can be made in the frequency range 50 Hz to 50 kHz as a function of temperature.

Experimental Design: Pyroelectric and Dielectric Constant

The detailed descriptions of the experimental measurement methods of the frequency and temperature dependent pyroelectric coefficient and dielectric constant discussed above are reviewed. Descriptions of the measuring circuit, probe assembly, sample mounting, and temperature measurements are successively summarized. The entire assembly has been checked using single crystal barium titanate ($BaTiO_3$) as a calibrant. Finally, the associated computer module for controlling the measurements and allowing on-line data reduction is summarized.

Measuring Circuit

A control panel has been built to house all the circuitry of the experiment which is shown in Figure 3. One cable connects the probe to the control panel. It contains two coax cables for each sample, one for each plate, as well as wires connecting to the resistance thermometers. A switch on the panel allows the selection of the sample to be measured. Both leads to the other two samples are grounded. Other switches allow the selection of the mode of operation; the pyroelectric measurement, or either of the dielectric measurement modes. The panel contains the Keithly model 301 electrometer operational amplifier and its power supply. Controls to adjust the zero offset are on the front panel.

The power supply for the resistance thermometers consists of a 22 1/2 volt battery in series with a 2.1 M Ω resistor. Also in series with these is a 250 K Ω variable resistor. The current through the resistance thermometer can be adjusted to 10 μA and the voltage drop measured. The resistors have been calibrated by Lake Shore Cryotronics Inc.

Probe Assembly

A drawing of our double can probe capable of taking the sample from 300 - 4.2 K is shown in Figures 4 and 5. Three samples are mounted in the sample holder (Figure 4) inside can A (Figure 5) which is 1 inch in diameter and 5 inches long. Can A may be evacuated or filled with exchange gas independent of the rest of the system. Can A is inside a larger can B (Figure 4) that may also be evacuated or filled with exchange gas. The larger can B is positioned at the bottom of a glass dewar, in contact with liquid helium. The temperature of can A may be raised above that of can B by means of a heating coil or being brought in thermal contact with the can B by introducing exchange gas into the outer can.

Sample Mounting

The three terminal capacitance measurement using the General Radio 1615-A bridge requires that the sample whose capacitance to be measured is encased in a grounded shield. Each sample contained between metal electrodes is placed in a small copper box, which is grounded. There are two holes in each box to pass the leads which are attached to each capacitor plate. The leads are then soldered to copper wires or connecting posts. The inside of each box is coated with G. E. Varnish to electrically insulate the sample from ground. The boxes are sufficiently large to accommodate samples 0.5 cm in diameter and up to 0.25 cm thick. Three sample boxes can be mounted inside the small can A at one time.

The temperature of the probe head inside can A is measured by means of two calibrated resistors from Lake Shore Cryotronics. One is

a 100 Ω platunum resistor which will be used in the temperature range from 30 - 300 K. The other is a 1000 Ω Germanium resistor that will be used in the region from 2 - 40 K. The resistors are attached t; the rack that holds the sample boxes with G.E. Varnish, which is an electrical insulator and a good heat conductor.

Computer Control

The measurements are currently being computerized using a PDP 11/03 minicomputer. The analog voltage signals from the thermometer and the operational amplifier are digitized using an analog to digital converter. The computer then performs simple manipulations to extract the dielectric or pyroelectric constant, depending on the mode of operation.

The computer system centers around a PDP 11/03 CPU with a dual drive floppy disk drive. One drive handles the system disk, making it possible to run the DEC RT-11 instruction set on the 11/03, while the other disk stores data and programs. Hard copies of the data and programs are provided by a DecWriter teletype, and a graphic output is provided by a Hewlett-Packard X-Y recorder. The data stored on the floppy disk is transferred onto a 9 - track tape at a central IBM 360 computer by a disk-tape converter, thus allowing complex data manipulations and computing on the larger IBM 360.

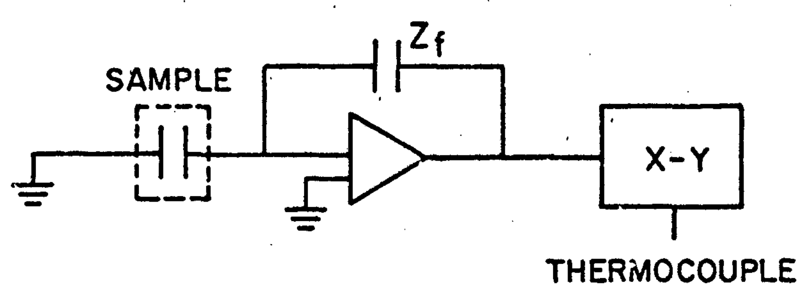
References

1. H. Kawai, Japan J. Appl. Phys. 8, 975 (1969).

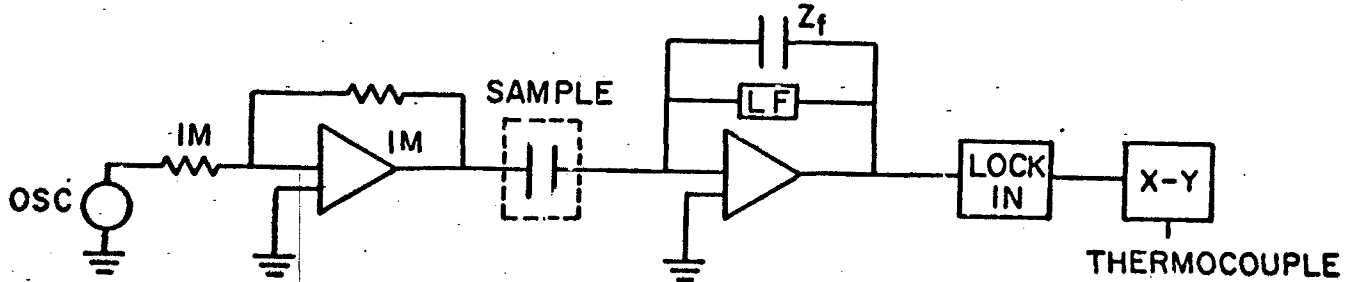
2. See, for example, A. M. Glass, J. Appl. Phys. 40, 4699 (1969).

3. Capacitance Bridge and Capacitance Measuring Assembly, General Radio Company (West Concord, Mass., 1963).

Figure Captions

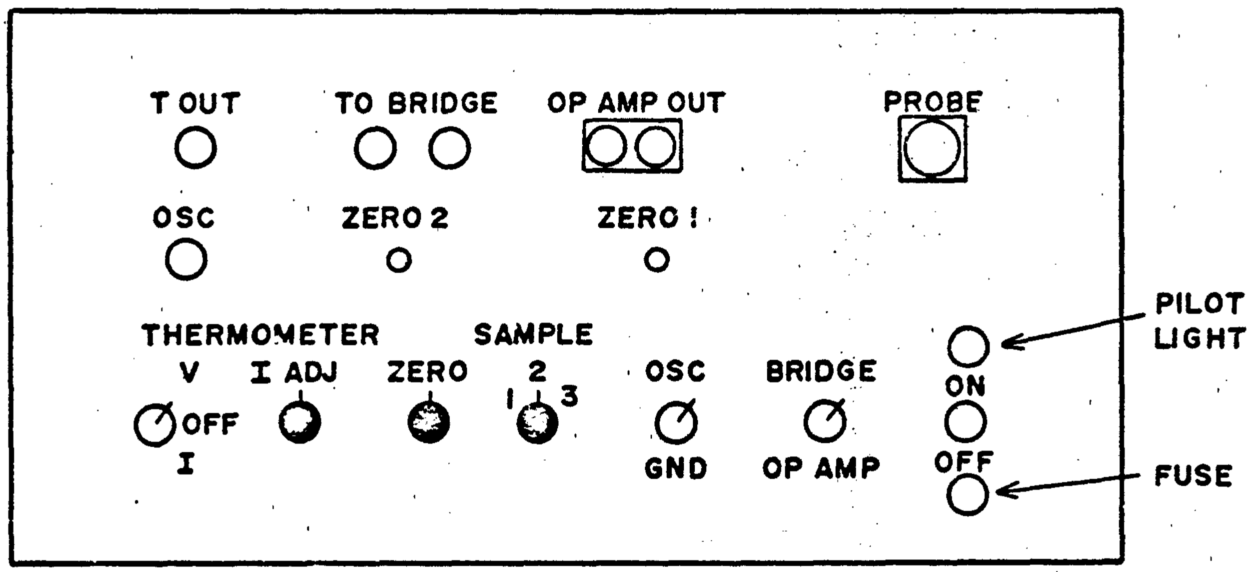


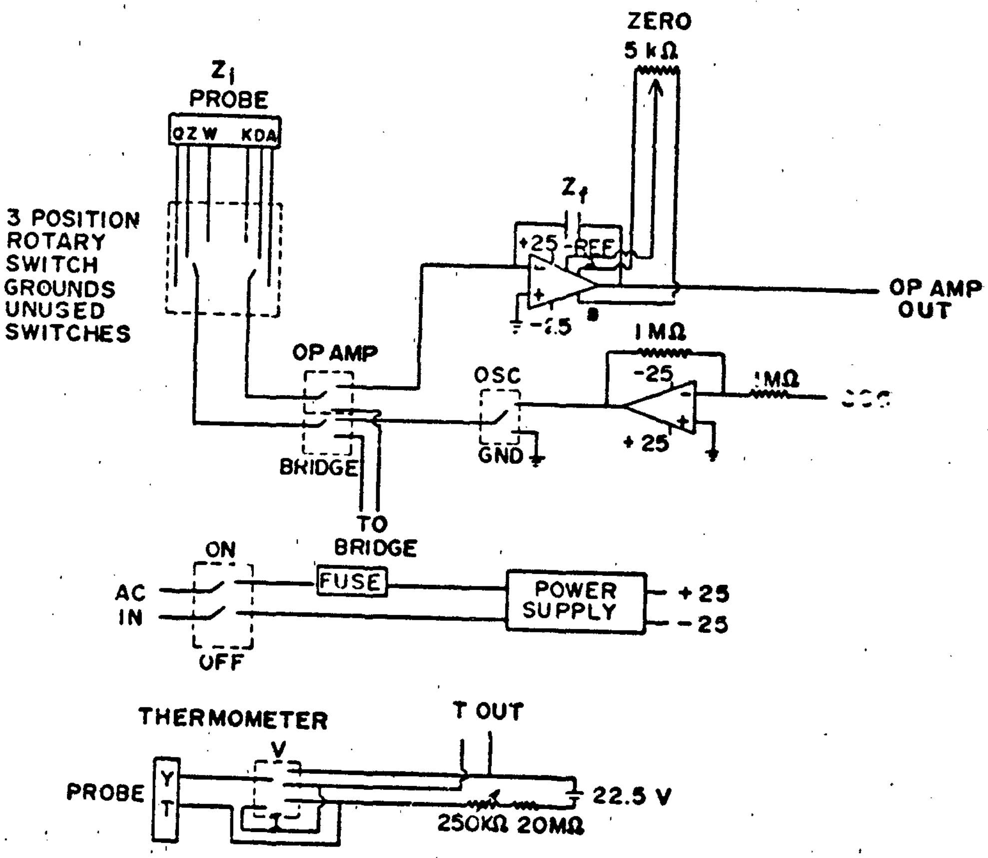
SAMPLE
Z_f
X-Y
THERMOCOUPLE



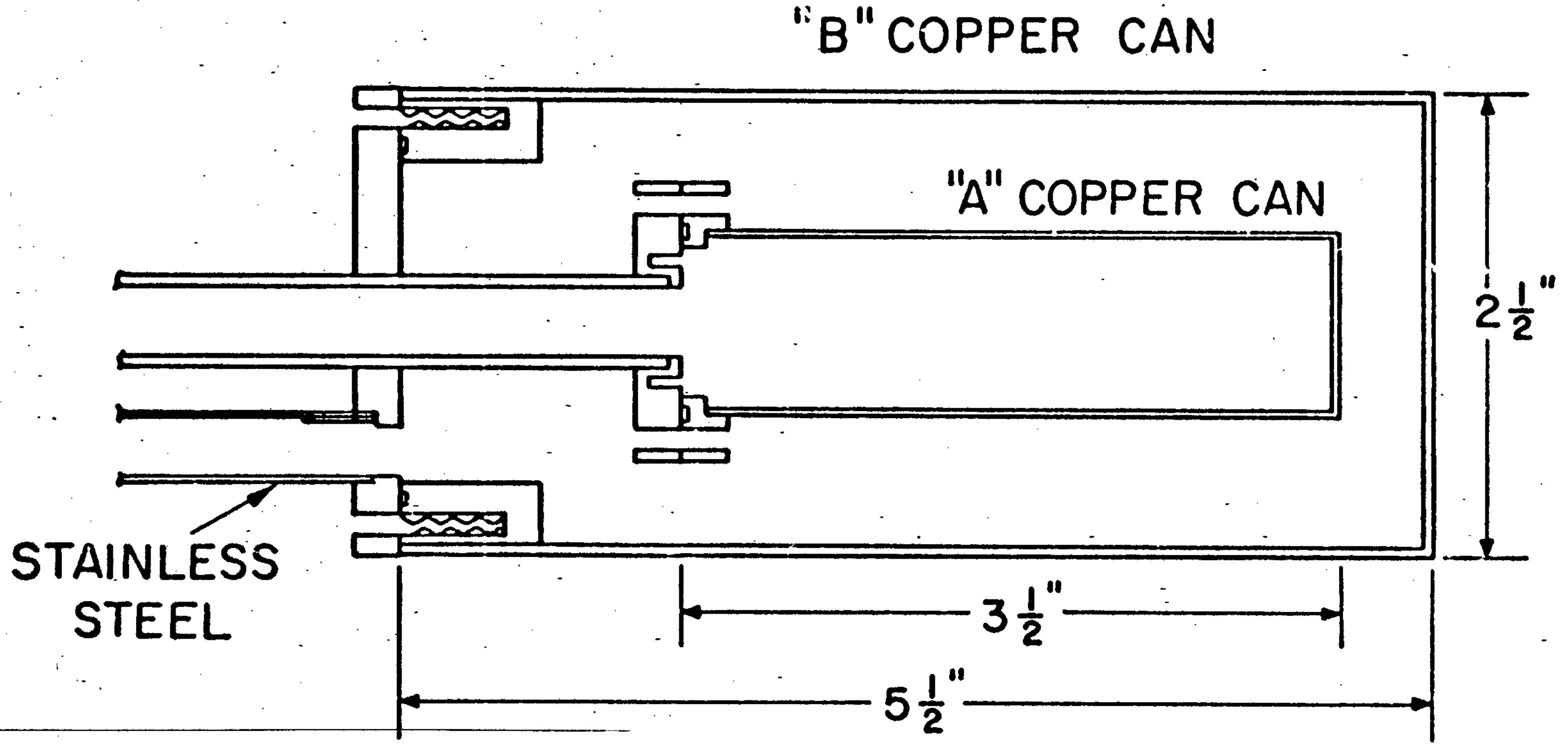
OSC
IM
IM
SAMPLE
Zf
LF
LOCK IN
X-Y
THERMOCOUPLE

CONTROL PANEL

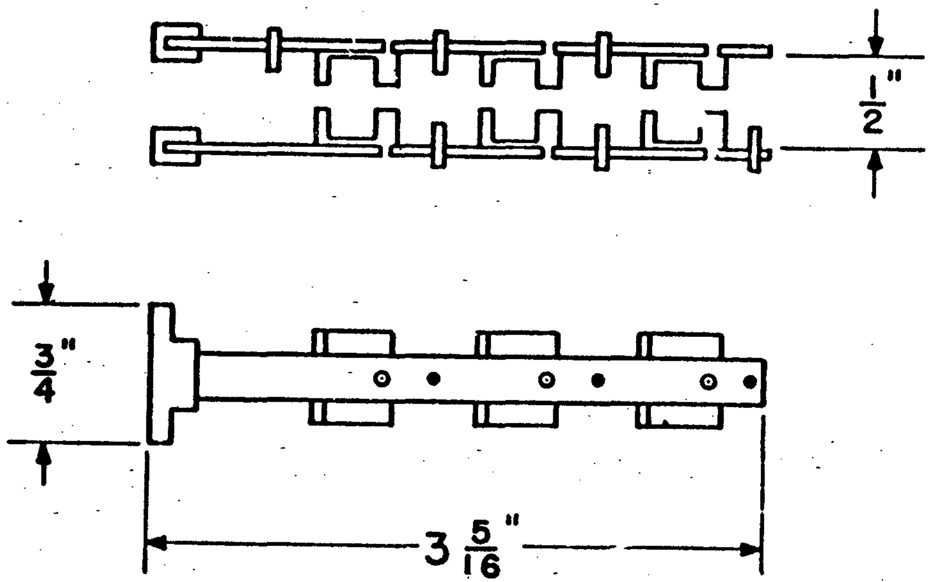




ZERO
5 kΩ
Z_i
PROBE
QZW
KDA
Z_f
+25
REF
-25
OP AMP
OUT
3 POSITION
ROTARY
SWITCH
GROUNDS
UNUSED
SWITCHES
1 MΩ
-25
1MΩ
OP AMP
OSC
GND
+25
BRIDGE
TO
BRIDGE
ON
AC
IN
FUSE
POWER
SUPPLY
+25
-25
OFF
THERMOMETER
T OUT
V
PROBE
Y
T
22.5 V
250KΩ 20MΩ



"B" COPPER CAN
"A" COPPER CAN
2 1/2"
3 1/2"
5 1/2"
STAINLESS
STEEL



1/2"
3/4"
3 5/16"

END

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